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Investigating the Effects of Different Collectors on Sulfide Minerals Kinetic Flotation of Miduk Copper Mine

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ABSTRACT

Miduk has sulfide copper mine and produces copper concentrate with an alloy of more than 30 percent. Flotation tests have been conducted using Sodium isobutyl ditiophosphate collectors (A3477) and sodium isopropyl xanthate (Z11) and thionocarbamate (X231). Denver cell flotation tests in laboratory scale are performed by injecting a type of collector at a dose of 35 gram/tone. Parameters such as recovery, alloy, using mineralogy results, kinetics constant in flotation reaction were measured for sulfide copper minerals (chalcopyrite chalcosite, covellite and pyrite). By comparing and analyzing the obtained results, it was determined by that collector A3477 with kinetics constant of 1.2285 (min^{-1}) has been more effective in floating copper and also has resulted in most alloy percentage; and with kinetic constant of 1.09878 (min^{-1}) had the highest kinetics constant for chalcopyrite mineral; and with kinetic constant of 1.6347 (min^{-1}) it has been the most effective collector in floating covellite comparing to Z11 and X231. X231 collector with kinetic constant of 1.42074 (min^{-1}) is the most effective collector in floating chalcosite mineral. Z11 collector has achieved a greater recovery of 95 percent. X231 and A3477 collectors had a better performance in pyrite abatement and have showed less selective properties toward flotation of pyrite.

Keywords: Flotation reaction kinetic constant; copper sulfide minerals; mineralogy process; Shahrbabak copper complex

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INTRODUCTION

Pulp chemistry in an operating unit is a complex system which yields the interactions of all additives such as different types of chemicals (collector, frothers, activators, inhibitor, PH regulator, etc.) and decomposability of ore materials. In mineral processing, chemicals are considered to be the integral part of the flotation process; so, being familiar with different materials and choosing the most effective ones in Pulp flotation is really important. Collectors are a group of heterogeneous compounds which are used to create a hydrophobic layer on the surface of minerals in Pulp flotation and provide the opportunity for recovery by attaching hydrophobic particles into air bubbles and using that opportunity to increase the floatation process [1].In many cases, Xanthate is being used as the primary collector for porphyry copper and molybdenum copper; whereas, there are different choices such as dithiophosphate,thionocarbamate, mercaptobenzothiazole, xanthigen formats for secondary collectors. Collector N-propyl-N-ethoxycarbonyl thiourea function (PECTU) is analyzed in order to recover copper from porphyry copper ore in laboratory and industrial scale in Dexing copper mine in china. The results showed that this collector has a very high selective ability for iron sulfide in medium alkaline environment(appromate 5/10 PH) [2] .Some laboratory scale researches has been conducted in Minto copper mine in Canada about simultaneous recovery of sulfide and oxide copper minerals using flotation. The used sample was a mixture of 70% sulfide copper and 30% oxide copper. Results showed that using –n octyl hydroxamate (AM28) with sulfide copper common collectors (potassium amyl xanthate) could recover oxide copper in a mixed sample; while, don't have the negative effects on sulfide copper recovery [3]. The effect of different mixtures of xanthate formats as collector in chalcopyrite, chalcosite, bornite, and covellite and pyrite flotation was considered. In addition to appropriateness of this collector for most of the sulfide copper, the results showed that it has other advantages in thiol common collectors (such as xanthate). Among these advantages, we can mention stability of these collectors in a wide range of PH (5 – 10/5) [4].

2 Material and Methods

Given that copper concentration plant victuals are being provided by 5 fronts; in order to simulate flotation supplies with plant supplies, the needed soil sample is taken from 5 active fronts that each is grind using laboratory jaw crushers and passed through a 2 millimeter sieve. After determining the alloy for each five samples, samples will be mixed according programs in order to obtain final sample. Soil blending specifications are presented in table 1

Table 1 Commixture rate of different fronts to supply

weight (kg)	alloy (%)	Front number
37	0.75	1
16	0.65	2
12.5	1.6	3
20	0.8	4
18.5	0.7	5

By applying the mentioned percentage, calculated grade of the supply is 0.87 percent which is close to the calculated grade of plant supply which is acceptable. Final mineralogy results are given in tables 2, 3, and 4.

Table 2 Amount of minerals in final supply

Amount (%)	name	Amount (%)	name
0.688	chalcosite	6.787	pyrite
0.19	covellite	0.043	limonite
0.272	chalcopyrite	0.105	sphalerite
92.642	non- metallic minerals	0.076	hematite
0.175	Oxide minerals	0.014	magnetite

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Table 3 Degree of freedom in final supply

Name	Degree of freedom
chalcosite	70.19
covellite	58.49
chalcopyrite	82.35
pyrite	75.07

Table 4 Minerals alloy in final supply

Alloy (%)	name
0.87	copper
0.1	Oxide copper
3.34	iron
0.005	molybdenum

2.1 Crushing Test

To calculate the needed crushing time in order to change the sample size into d_{80} equals 100 micron, 1420 gram sample and 1420 gram water are added into the Jar Mill and 12 minutes of crushing time is applied. Pulps in the mill are then being unloaded and after drying up, sieve analysis is being performed. According to the obtained d_{80} at 12 minutes. The above steps will be performed at 15 and 18 minutes as well. The best crushing time was 17.40 minutes. Figure 1

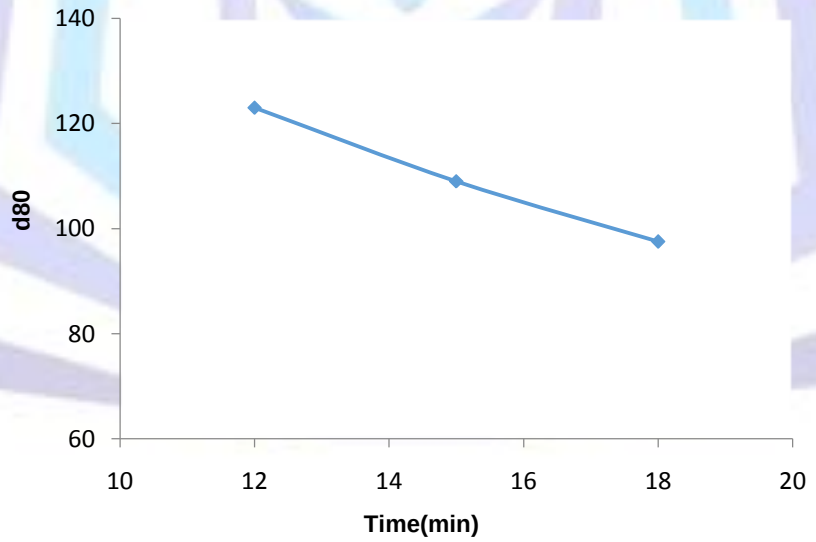

Fig.1. D80 curve toward final supplies crushing time

2.1.1. Laboratory scale comparative flotation tests

In Shahrbabak copper complex's procreator model, three types of collectors, xanthate (Z11), dithiophosphate (A3477) and thionocarbamate (Flomin) are being used. Frothers being used are as follow: polypropylene glycol (A65) and methyl isobutyl carbonyl (A70). Like most porphyry copper plants, lime is used as PH regulator.The amount of chemicals being used frequently depends on input soil behavior –it varies sometimes- but according to control room data and annual reports, the average amount of chemicals are 5gram/ton for Z11, 10 gram/ton for A3477, 22 gram/ton for Flomin, 10 gram/ton for A65, and 8 gram/ton for A70 [5].

2.1 .2 Kinetic Test

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Kinetic test was used to determine the best time for skim in comparative tests. First, pulps are prepared according to the needed solid degree. Then, using Denver cell in laboratory scale, regulating the PH, and adding the chemicals and needed time according to schedules, aeration will be applied. And drawing the recovery curve at time is the last step (figure 2). With regard to the momentary alloy, the momentum alloy from 10 minute concentrate gets closer to the supply alloy; so the best time is 10 minutes.

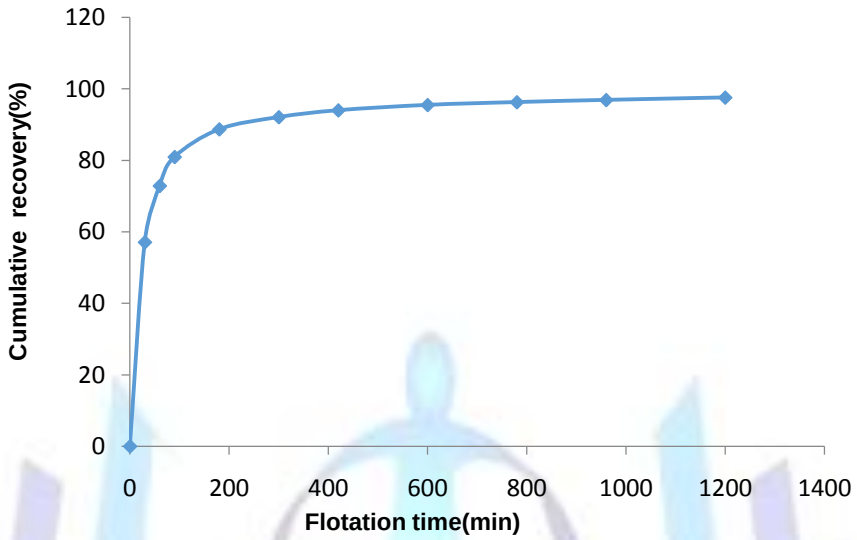

Fig 2. Changes in recovery toward kinetic test time

In order to conduct comparative tests for the collectors X231, A3477, Z11; each collector gets the dose of 35 gram/ton – because the total gram/tone in the plants supply is 36 gram/ton-, and only one collector is selected for the flotation test. For frothers, 10 gram/ton for A65, and 10 gram/ton for A70 are being used according to the plant characteristics. Skim had done in 6, 2, 10 minutes. After drying and weighting, the collected concentrates in different moments get chemical analysis. Laboratory test terms are given in table 5.

Table 5. Terms of Denver's laboratory cell test

retemarap	eulav	retemarap	eulav
ore mass, dry basis(gram)	1420	Nominal capacity of Denver cell(L)	3
Percentage of solids(w/w)	30.0	Stirring speed(rpm)	1250
pH	11.5	Total flotation time(min)	10

2.2 Mineralogy analysis

Sulfide and copper minerals flotation properties differ according to the nature of ores. Mineralogical properties of mineral impurities, changes in crystal structure, other gangue minerals and degree of freedom are the factors that affect minerals flotation properties; chalcosite (CU_2S) is based on chemical formula with 79.8 percent copper and 20.2 percent sulfur. Its hardness is between 2 to 3 and its weighs is 5.5. In many porphyry copper and copper – molybdenum ores are primary mineral and chalcopyrite, bornite, and covellite are secondary minerals. Chalcosite may be converted into malachite and azurite either partially or totally, that's why oxide copper zone could be seen in most of porphyry copper ores. Like covellite, chalcosite tends to produce soft parts during crushing process that causes problem in retrieving it. This mineral floats easily by xanthate and dithiophosphate or thionocarbonate as a secondary collector. In almost every porphyry copper ores processing operations associate with chalcosite, it is necessary to use secondary collector and xanthate together [6]. In order to perform mineralogy analysis, some tablets and section preparation device were produced and are being used for mineralogy studies. Concentrate and wastes instructions for this device are the same; the only difference is

the amount of weighted sample for analysis; mixture of 0.5 gram concentrate and 11.5 gram for Bakelite powder (binder); and mixture of 7 gram for waste and 7 gram for Bakelite powder. After placing the mixture in the press machine, model: SIMPLIMENT3000, tablets will be produced. Then, the tablets will ground in polishing system, model: ROPOLPET, in multiple steps so that the level of minerals will be determined and the results will be used for mineralogy studies.

3. Results and Conclusions

In ore arrangement operation weighting F, if we presume that the production of a product weights C and a waste weights T and the grades for these three parts are respectively c, f, and t; then the ratio of adorned product alloy to the primary alloy is called ratio of enrichment [7].

$$E = \frac{C}{F} \tag{1}$$

Due to the need for balancing, weight and alloy are as follow:

$$F = C + T \tag{2}$$

$$Ff = Cc + Tt \tag{3}$$

By eliminating parameter T between two above equations, we will have:

$$\frac{F}{C} = \frac{(c-t)}{(f-t)} \tag{4}$$

Coefficient ratio is called arrangement.

Efficiency (recovery) operations means valuable mineral's weight ratio in arranged product to its value in its primary load is equal to:

$$R = 100 * \frac{c.(f-t)}{(f.(c-t))} \tag{5}$$

Alloy for High graded product and its recovery are parameters which are associated with each other for technical assessment of arrangement method. Nevertheless, comparison between the two arrangements using these two parameters could encounter difficulties. Hence, indexes called "separation efficiency" (*SE*) is defined to convert these two parameters into an index.

$$SE = \frac{(c(f-t)(c-f)(100-t))}{(f(c-0.1)^2(100-f))} * 100 \tag{6}$$

However, the separation efficiency is useful for comparing different situations, this parameter has no connections to economical parameters, and high separation efficiency does not necessarily represent the best economical point of view. Considering the fact that the purpose of this ore arrangement is to increase the economic value of minerals. It is necessary to choose a combination of alloy and recovery; so that, it can provide additional stats for every tone of array materials. Increasment in alloy leads to the decrease in recovery that would cause the loss of additional stats. In contrast, the increase in recovery requires the alloy reduction that leads to the increasment in transportation and melting. According to recovery curves, in figures 3, 4, 5 and alloy curve – used collectors recovery in figure 6, collector Z11 had more recovery, but collectors A3477 and X231 respectively had higher alloy toward collector Z11. Results showed that using collector Z11 has negative effect on the alloy itself and causes alloy

Table 6. Separation efficiency of used collectors

collector	S.E
A3477	80.42
Z11	78.5
X231	76.5

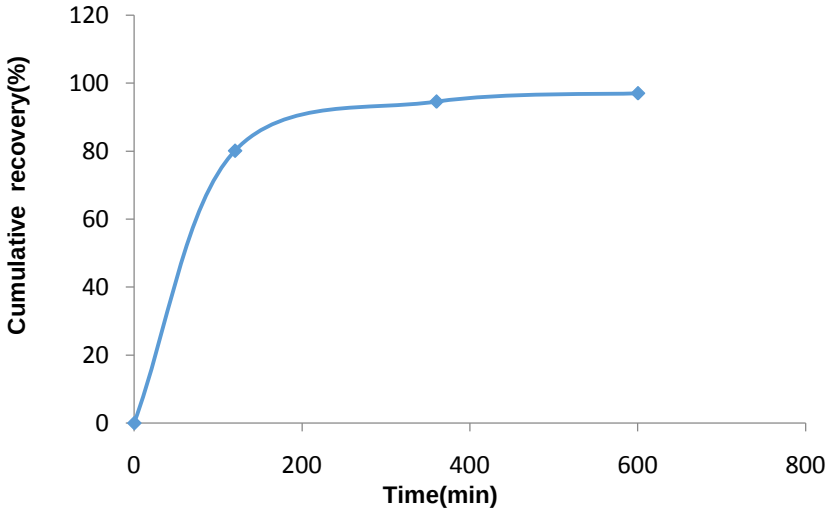

Fig 3. Recovery curve toward time collector Z11

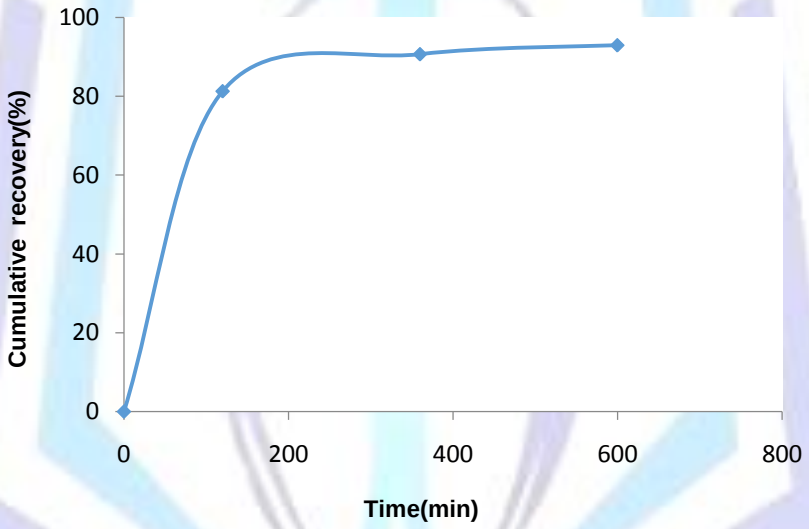

Fig 4. Recovery curve toward time collector X231

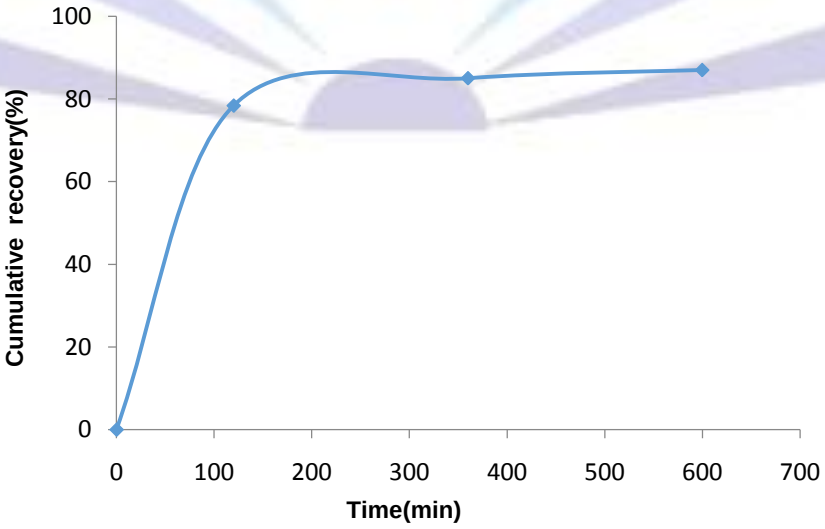

Fig 5. Recovery curve toward time collector A3477

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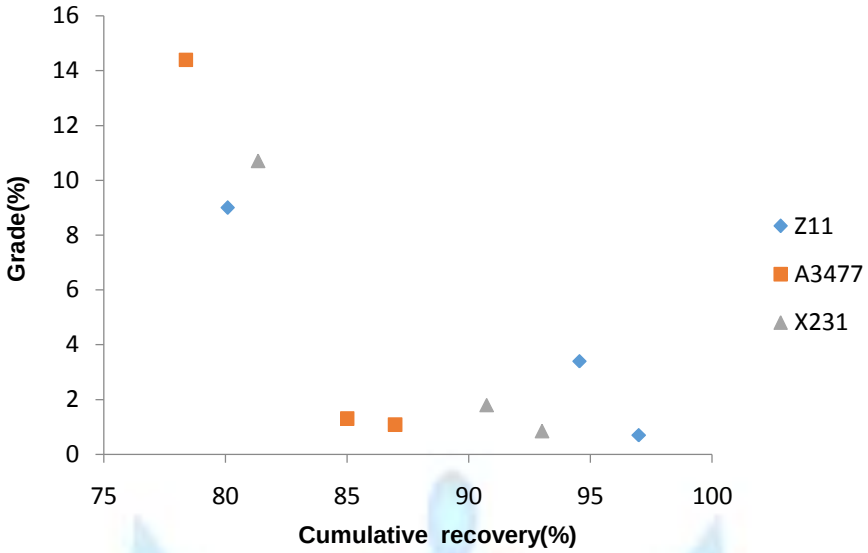

Fig 6. Curve Alloy – recovery, used collectors

3 .1 Kinetic flotation

Studying particles flotation rate in flotation operation is called kinetic operation analysis. And kinetic constant K shows a quantitative measurement of likelihood of a mineral recovery in concentrate. This constant is measured and compared for different collectors.

3.1.2 Measurement of kinetic constant of sulfide copper and copper minerals

There are two methods for measuring kinetic flotation constant: using solver option in Excel and passing best lines from points. In this method, using first-order kinetic, the flotation kinetic constant and the amount of long term recovery are obtained as the sum of least square of errors is minimized. Another method is the conventional method; that is, calculating recovery line graph slope is based on time which is the kinetic floatation constant [8].

$$K = \left(\frac{1}{t}\right).\ln\left(\frac{R\infty}{(R\infty - R(t))}\right) \quad (7)$$

To select the best operating condition in terms of chemical or tools, we can use R_∞ and K (by determining these two parameters for different conditions, the best will be chosen according to operating situations). K represents flotation ratio and if there was no problem in the cell, there would be no limitation as well. In order to evaluate the effect of one agent in each step, we should calculate R_∞ and K and decide about changing procedure according to these two criteria. After conducting mineralogy analysis using results from mineralogy, recovery curve – time was drawn for sulfide copper minerals and each collector. Figure 7-9. The results were used to compare the performance of different collectors toward flotation parameters.

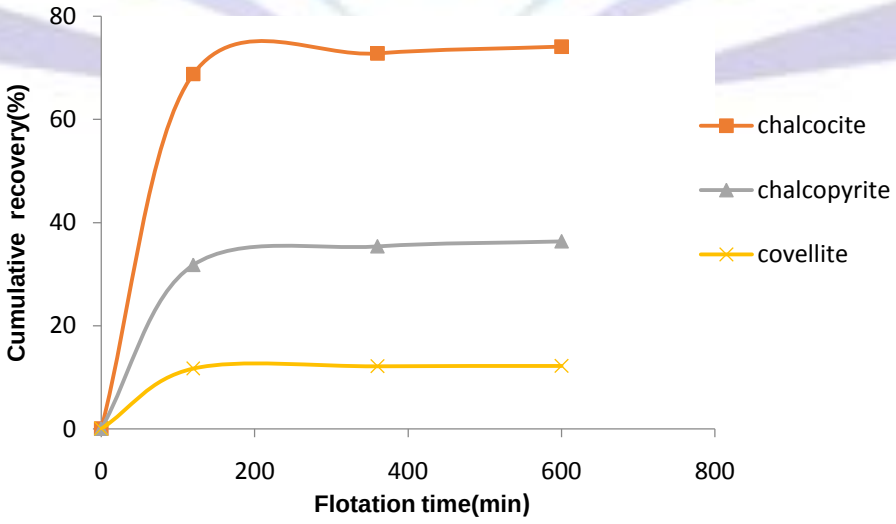

Fig.7. Curve Recovery –time, sulfide copper minerals flotation for collector A377 test

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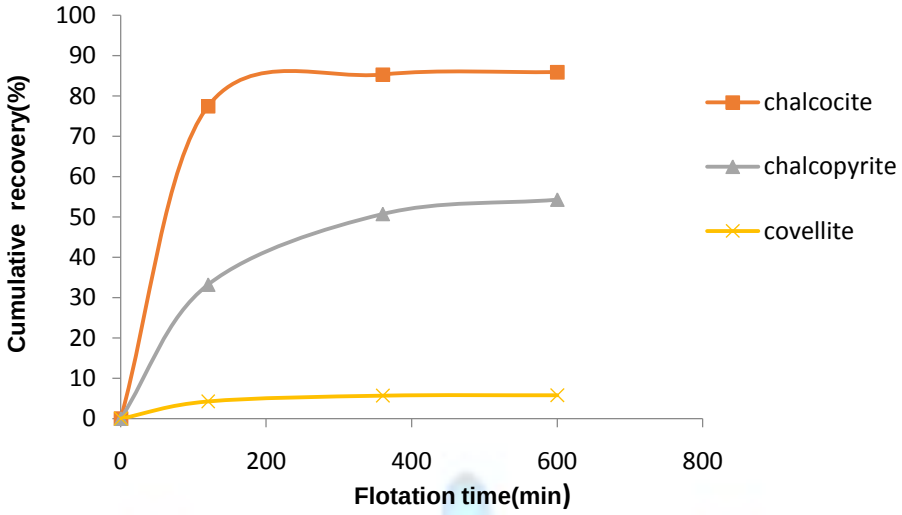

Fig.8. Curve Recovery – time, sulfide copper minerals flotation for collector Z11 test

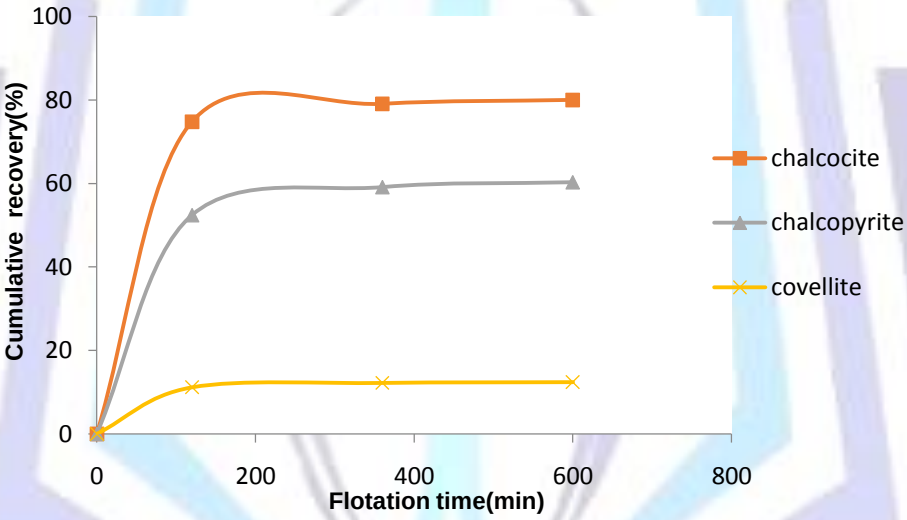

Fig.9. Curve Recovery –time, sulfide copper minerals flotation for collector X231 test

With mineralogy results, maximum recovery of sulfide copper and kinetic constant (chalcosite, chalcopyrite, covellite) for various collectors were compared using excel and presumption of primary model fi flotation reaction was measured and compared. Table 7-9.

Table.7. Collector Z11 test results for kinetic sulfide minerals

	k (min^{-1})	R_∞
chalcosite	1.1769	85.5688
chalcopyrite	0.47124	54.3151
covellite	0.66174	5.833
total copper	0.906	95.6764

Table.8. Collector A3477 test results for kinetic sulfide minerals

	k(min^{-1})	R_∞
chalcosite	1.3996	73.257
chalcopyrite	1.09978	35.755
covellite	1.6347	12.157
Total copper	1.2285	85.6987

Table.9. Collector X231 test results for kinetic sulfide minerals

	k (min^{-1})	R_∞
chalcosite	1.42074	79.399
chalcopyrite	1.0569	59.6073
covellite	1.19364	13.3384
Total copper	1.09404	91.59856

Collector A3477 with kinetic constant 1.2285(min^{-1}) is more effective in copper flotation comparing to collectors Z11 and X231. Also, collector A3477 with kinetic flotation constant of 1.09878 (min^{-1}) is more effective in chalcopyrite flotation and also with kinetic constant of 1.6347 (min^{-1}) is more effective in covellite flotation comparing to collectors Z11 and X231. Collector X231 with kinetic constant of 1.42074 (min^{-1}) is more effective in chalcosite mineral flotation. According to the results, after collector A3477, collector X231 is more effective in sulfide minerals flotation. But, collector Z11 had more recovery.

3.2 Pyrite inhibitor

Pyrite considered as a troublous mineral that produces problems in both copper ore flotation, and sulfide ore flotation. The main reason for declining grade is pyrite. [9].Pyrite's weight percentage in flotation concentrate and waste tests for chemicals was compared. According to the results from pyrite's weight percentage in flotation concentrate and waste tests, collector X231 had the least amount of pyrite in final concentrate. Due to adverse effect of pyrite on concentrates alloy, one of the reasons of higher alloy in collectorsA3477 and this collector is their great performance on acting as pyrite inhibitors. But Z11 collectors showed higher percentages of pyrite. Also, using results from mineralogy, curves in pyrite recovery were drawn and the effect of collectors on pyrite flotation kinetic was analyzed.

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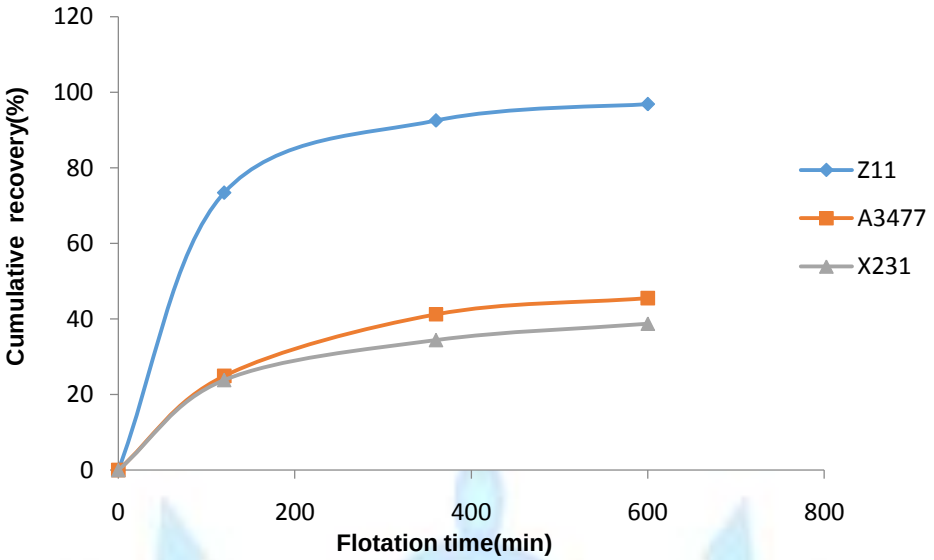

Fig 10.Recovery curve- pyrite flotation time. For collectors X231, Z11 and A3477

According to obtained R_{∞} and K values from solver in Excel for pyrite flotation, figure 10 and table 10 were created. Collector Z11 operated more effective in pyrite flotation by having kinetic constant of 0.738 (min^{-1}) and its poor performance on pyrite related inhibitions, the concentrate grade were decreased.

Table.10. Pyrite flotation kinetic results and concentrate and waste analysis in flotation tests

collector	K(min^{-1})	R_{∞} (%)	Alloy wastes (%)	Pyrite alloy in cons (%)
Z11	0.738	94.836	0.994	44.87
X231	0.498	37.384	5.631	19.49
A 3477	0.384	46.092	6.047	28.69

4. Summation

Crushing tests in laboratory showed that the time needed to reach to d_{80} equals 100 micron, is 17.5 minutes. According to kinetic tests, the best time for optimizing chemicals concentrations flotation tests in laboratory scale is 10 minutes. The concentrate from conducted flotation test with collector A3477 had the highest grade comparing to other collectors in flotation test capable of injection. Using excels optimization choice and assuming a primary model for flotation reaction of collector A3477 with kinetic constant of 1.2285 (min^{-1}), it was the most effective collector in copper flotation. Collector A3477 with kinetic constant of 1.09878 (min^{-1}) was the most effective collector for chalcopyrite flotation, and with kinetic Constance of 1.6347 (min^{-1}) had the highest kinetic Constance for covellite flotation. Collector X231 with the kinetic constant of 1.42074 (min^{-1}) is the most effective collector in mineral chalcosite flotation. Given that chalcosite mineral has a significant effect on increasing the alloy, collector X231 is one of the reasons for a good alloy in chalcosite flotation comparative test. Collector Z11 with a high pyrite percentage in more effective in its flotation and acted poorly in inhibition part that was the reason for reduced alloy. A3477 collectors had better performance in pyrite related inhibition and have less selective choices toward pyrite flotation that is a representation of dithiophosphate good operation in pyrite related inhibitions. Also, collector X231 performance in pyrite related inhibitions was satisfying after A3477.

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